

Quasi-parity-conserving octahedral model for (H,Be) and (D,Be) tunneling complexes in silicon

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A six-site (octahedral) tunneling model is presented for the (H,Be) and (D,Be) acceptor complexes in silicon. Parity has been found to be, in the approximation used to describe these systems, a conserved quantity. With parity conservation, the model yields spectra that fit the available experimental data with accuracy similar to the previously proposed four-site (tetrahedral) model, but which do not exhibit the unexplained discrepancies—present in the tetrahedral model—between the tunneling frequencies of the complexes and the rotational frequencies of the corresponding diatomic molecules.

I. INTRODUCTION

Hydrogen-beryllium and deuterium-beryllium acceptor complexes in silicon have been experimentally identified as tunneling systems by Muro and co-workers.^{1,2} Their infrared and far-infrared spectra are essentially explained by the theory of Haller and co-workers³⁻⁶ that considers the diatomic complex as a hindered rotator. This picture is equivalent to assuming, for the specific case under consideration here, that the proton or deuteron is delocalized and tunneling between equivalent, low-symmetry positions about the substitutionally located Be atom. In their specific model, Haller, Joós, and Falicov³ used the minimal set of equivalent positions, i.e., four tetrahedral sites around the Be atom, corresponding to either the bonding or the antibonding directions of the silicon structure. Based on this geometry, they developed a model in which the local tetrahedral environment was characterized by the T_d point group, a group which does not include inversion symmetry.

Peale, Muro, and Sievers² fitted the parameters of this theory to explain their experimental results. The data were satisfactorily reproduced with parameters which were all in an acceptable range of values. There was, however, a fundamental inconsistency in the model as it stood. The parameters include electronic- and nuclear-energy matrix elements, which can be extracted from the optical data. From the obtained parameters² it was found that excited levels of the acceptors (H,Be) and (D,Be) in silicon exist in pairs separated by a tunneling energy with values 38.8 cm^{-1} for (H,Be) and 16.2 cm^{-1} for (D,Be). However, for the freely rotating (H-Be)⁻ molecule, the energy separations between the $J=0$ and $J=1$ rotational levels are 21.1 cm^{-1} for (H,Be) and 11.6 cm^{-1} for (D,Be), if it is assumed that the bond length of the defect in Si is the same as in the free neutral⁷ molecule ($r = 1.333 \text{ \AA}$). These values for energy separations of rotational levels are *less* than the observed separation of the tunneling levels, although the free rotation should be the *upper* limit: the tunneling (hindered rotation) becomes more rapid for molecules constrained by the crystal potential (i.e., a less hindered, freer rotator).

There have been several calculations^{8,9} of total energies

for a variety of configurations of hydrogen-impurity pairs in elemental semiconductors. Denteneer, Van de Walle, and Pantelides⁸ found that the bonding direction (tetrahedral configuration) contains always an energy zero-gradient point [labeled BM (bond minimum)] for the hydrogen locations in all complexes in both Si and Ge. They also find a second set of energy zero-gradient points (labeled C in Ref. 8) located along the six equivalent cubic $\langle 100 \rangle$ directions. For the particular case under consideration here—(H,Be) in silicon—Denteneer, Van de Walle, and Pantelides found that the *global* energy minima occur for the hydrogen (either H or D) at C , located at a distance of approximately 1.50 \AA from the Be center along the $\langle 100 \rangle$ directions; the Be atom relaxes approximately 0.14 \AA from the original Si site, away from the hydrogen. The $\langle 111 \rangle$ type, bonding-direction BM zero-gradient points are saddle-point singularities with energy 0.1 eV above the energy of the C minima. They also find that the possible tunneling paths¹⁰ between the C minima do not involve the BM saddle points, for which the tunneling barrier would be much too high. The tunneling path goes through the *antibonding* directions and has a barrier height estimated to be 0.4 eV . These numbers are consistent with the possibility of the hydrogen atom tunneling among the six different C equivalent positions and avoiding the four (tetrahedral) BM sites altogether.

If the above picture is correct, a reanalysis of the tunneling model is needed. It is important to see whether the hindered rotator with energy minima at the six C sites can explain the experimental data. The present contribution contains this analysis and the results obtained are not only compatible with experiment, but they also eliminate the inconsistency with the molecular data quoted above.

II. CALCULATION AND RESULTS

The symmetry of the octahedral complex center—shown in Fig. 1—requires careful discussion.¹¹ The octahedron defined by the six equivalent configurations of the Be atom with the hydrogens along $\langle 100 \rangle$ directions is invariant under the operations of the O_h group. The presence of the Si nearest and more distant neighbors

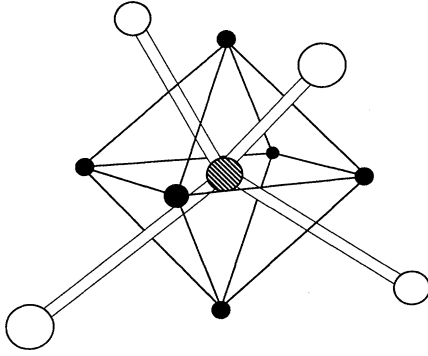


FIG. 1. The geometry of the complex in the octahedral configuration. The Be-atom position is the hatched circle; the hydrogen six tunneling positions are the black circles and the Si nearest neighbors are shown as open circles.

reduces that symmetry to the well-known T_d symmetry of all atomic sites in the diamond structure. It should be remembered that O_h contains the inversion operation, whereas T_d does not. In fact the group O_h can be expressed as the direct-product group of T_d with the inversion group. The irreducible representations of O_h are therefore twice as many as those of T_d , and can be labeled by Γ_i^\pm , with the Γ_i indicating the irreducible representations of T_d , and the \pm superscript indicating the properties under inversion.

It should also be remembered that even though the point group operations in the diamond lattice at the atomic sites, $a(0,0,0)$ and $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, do not include the inversion, the *space group* of the diamond lattice contains the inversion at points in the middle of the Si—Si bonds, $a(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, and at the center of the octahedral holes, $a(\frac{5}{8}, \frac{5}{8}, \frac{5}{8})$, and therefore the Bloch states are labeled by a \pm index that denotes parity about these centers. *These parity labels are of no relevance for the present purposes and should be ignored altogether.*

The top of the valence band in Si and Ge, however, is formed *exclusively* by functions which have *p*-like symmetry about the individual atoms. These functions are, to a first approximation, of negative parity about each atom, even though that parity character is broken away from the center, as the nearest neighbors are approached. Therefore, if (i) the electronic wave function of the center is described exclusively by the product of a smooth envelope and a linear combination of the six spinors from the top of the valence band; and (ii) crystal-field corrections arising from neighboring Si atoms are neglected; then *parity* in the total wave function, with respect to the center of the complex, *is a good quantum number.*

Put in different terms, O_h symmetry is imposed by the model on the system to a very good degree of approximation, even though the true symmetry is only T_d . The quasi-parity-conservation imposes new selection rules, which make some of the otherwise-allowed transitions now forbidden (in reality only very weakly allowed), and reduces the number of possible optical lines.

Following Ref. 3, the Hamiltonian of the complex for

the electronic and nuclear degrees of freedom is expressed by

$$H = H_a + H_N + V, \quad (1)$$

where H_a describes a hole bound to an ordinary isocoric hydrogenic acceptor, H_N the dynamics of the internal (nuclear) degree of freedom of the complex, and V the interaction between both degrees of freedom. The nuclear dynamics of the complex is described in the Hilbert space defined by localized nuclear functions centered at the six equivalent $\langle 100 \rangle$ configuration energy minima C . They are denoted by the symbols $|I\rangle$, with $I=1,2,\dots,6$, for the functions located at sites along the $[100]$, $[\bar{1}00]$, $[010]$, $[0\bar{1}0]$, $[001]$, and $[00\bar{1}]$ directions, respectively. With this basis, H_N can be written as the 6×6 matrix

$$\begin{pmatrix} E_N & 0 & -t & -t & -t & -t \\ 0 & E_N & -t & -t & -t & -t \\ -t & -t & E_N & 0 & -t & -t \\ -t & -t & 0 & E_N & -t & -t \\ -t & -t & -t & -t & E_N & 0 \\ -t & -t & -t & -t & 0 & E_N \end{pmatrix},$$

where t is the hydrogen (H or D) tunneling matrix element between nearest-neighbor octahedral configurations. The effect of tunneling between second-nearest-neighbor configurations may be neglected. Diagonalization of this matrix yields three energy levels: a Γ_1^+ singlet, with nuclear energy $E_N - 4t$; a Γ_5^- triplet, with energy E_N ; and a Γ_3^+ doublet, with energy $E_N + 2t$. The singlet and the doublet have even parity; the triplet is odd. In the free-rotator limit the Γ_1^+ singlet arises from $J=0$ state; the Γ_5^- triplet comes from the $J=1$ states; the Γ_3^+ doublet is derived from two states from the $J=2$ quintet which, under the O_h symmetry split off to a lower energy, leaving behind a much higher (and inaccessible) Γ_5^+ triplet

$$J=2 \rightarrow \Gamma_3^+ \oplus \Gamma_5^+.$$

It should be noted that positive values of t correspond to the same ordering of levels as in the rigid rotator, i.e.,

$$E(J=0) < E(J=1) < E(J=2)$$

or

$$E(\Gamma_1^+) < E(\Gamma_5^-) < E(\Gamma_3^+),$$

whereas negative values yield the reverse ordering; as seen below the experimental data are consistent with positive t .

The next step is to consider the complete ground-state manifold: (1) the four electron states derived from the product of (a) the $1s$ hydrogenic envelope and (b) the four spinors corresponding to the Γ_8 Bloch states at the top of the Si valence band; (2) the nuclear states defined by the six octahedral C positions; and (3) their dynamic interactions (i.e., the correction to the Born-Oppenheimer approximation). There are all together 24 states of the combined electronic-nuclear degrees of freedom.

The electronic ground-state manifold of an ordinary

acceptor, defined by the first term H_a in Eq. (1), is fourfold degenerate, with energy E_{1s} . Its eigenfunctions transform like the $J = \frac{3}{2}$ spin states of a p orbital, i.e., according to the Γ_8^- representation of O_h . The corresponding states are denoted by $|m\rangle$, with $m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. The complete set of the 24 states that cover the ground-state electronic-nuclear manifold is therefore identified by $|Im\rangle$, where

$$|Im\rangle = |I\rangle \otimes |m\rangle .$$

The matrix elements of the various components of (1) in this basis are given by (i) the diagonal matrix elements

$$\langle Im|H_N + H_a|Im\rangle = E_N + E_{1s} ; \quad (2)$$

(ii) the off-diagonal matrix elements of H_N for I and I' nearest neighbors

$$\langle Im|H_N|I'm'\rangle = -t\delta_{mm'} ; \quad (3)$$

(iii) the matrix elements of V can be expressed in terms of two reduced matrix elements:

$$\langle Im|V|Im'\rangle = V_0 C(I; m, m') , \quad (4)$$

for the same nuclear location I , and

$$\langle Im|V|I'm'\rangle = V_1 D(I, I'; m, m') , \quad (5)$$

for I and I' nearest neighbors.

In the equations above V_0 is the central-cell-potential contribution; V_1 is a combined electronic-nuclear potential, which measures the breakdown of the Born-Oppenheimer approximation. In addition $C(I; m, m')$ and $D(I, I'; m, m')$ are generalized Clebsch-Gordan coefficients corresponding to the symmetry of the O_h group, and obtained as in Ref. 3.

The 24×24 matrix can be diagonalized in a straightforward way with the use of group-theoretical techniques. It corresponds to the reduction of the direct-product space

$$(\Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_5^-) \otimes \Gamma_8^- = \Gamma_6^+ \oplus \Gamma_7^+ \oplus 2\Gamma_8^+ \oplus \Gamma_6^- \oplus \Gamma_7^- \oplus 2\Gamma_8^- , \quad (6)$$

i.e., four doubly degenerate, fully diagonalized eigenvalues of symmetries Γ_6^\pm and Γ_7^\pm , and two sets of 2×2 secular equations which yield four sets of quadruply degenerate Γ_8^\pm states.

The eigenvalues are

$$E(\Gamma_6^+) = E_N + E_{1s} + \frac{2}{3}V_0 + 2V_1 , \quad (7a)$$

$$E(\Gamma_6^-) = E_N + E_{1s} + 2t , \quad (7b)$$

$$E(\Gamma_7^+) = E_N + E_{1s} + 2V_1 , \quad (7c)$$

$$E(\Gamma_7^-) = E_N + E_{1s} + 2t + \frac{2}{3}V_0 - \frac{8}{3}V_1 , \quad (7d)$$

$$E(\Gamma_8^+) = E_N + E_{1s} + \frac{1}{3}V_0 - V_1 \pm [(\frac{1}{3}V_0)^2 + (V_1)^2]^{1/2} , \quad (7e)$$

$$E(\Gamma_8^-) = E_N + E_{1s} - t + \frac{1}{3}V_0 + \frac{2}{3}V_1 \pm [(\frac{2}{3}V_1 + \frac{1}{3}V_0)^2 + (2V_1 - 3t)^2]^{1/2} . \quad (7f)$$

The electronic excited hole states, accessible by infrared optical excitations, all have a p -like envelope function. These states have zero electronic amplitude in the neighborhood of the nuclear sites, and it is reasonable to take V_0 and V_1 to be in this case negligibly small. In that case the electronic and the nuclear degrees of freedom decouple, and this decoupling results in each excited p -like hole state—with a degeneracy either $d = 12$ or 6 corresponding to the threefold degeneracy of the p -like envelope and either the fourfold degeneracy of the Γ_8 , or the twofold degeneracy of the Γ_6 symmetry of the Bloch states at the top of the valence band of silicon—coexisting with the three different nuclear levels described above. The energies of the excited states and their degeneracies are¹²

$$E_{\text{excited}}(N; \Gamma_1^+) = E_N + E_{np} - 4t , \quad (8a)$$

$$d_{\text{excited}}(p_{\frac{3}{2}}; N; \Gamma_1^+) = 12 , \quad (8b)$$

$$d_{\text{excited}}(p_{\frac{1}{2}}; N; \Gamma_1^+) = 6 ; \quad (8c)$$

$$E_{\text{excited}}(N; \Gamma_5^-) = E_N + E_{np} , \quad (9a)$$

$$d_{\text{excited}}(p_{\frac{3}{2}}; N; \Gamma_5^-) = 36 , \quad (9b)$$

$$d_{\text{excited}}(p_{\frac{1}{2}}; N; \Gamma_5^-) = 18 ; \quad (9c)$$

$$E_{\text{excited}}(N; \Gamma_3^+) = E_N + E_{np} + 2t , \quad (10a)$$

$$d_{\text{excited}}(p_{\frac{3}{2}}; N; \Gamma_3^+) = 24 , \quad (10b)$$

$$d_{\text{excited}}(p_{\frac{1}{2}}; N; \Gamma_3^+) = 12 . \quad (10c)$$

In the above equations ($N; \dots$) indicates the symmetry of the nuclear part of the direct-product function, and d denotes the total degeneracy of the particular level.

III. DISCUSSION AND CONCLUSIONS

The model presented above for all states—ground-state manifold and optically excited hole states—is restricted to electronic states derived from envelopes with well-defined spherical symmetry and from silicon p -like functions (Bloch states at the top of the silicon valence band), and nuclear states derived from tunneling between six octahedrally located sites. In this approximation inversion symmetry—or its mathematically equivalent symmetry in the Hamiltonian matrices—introduces a new conserved quantity. Since (i) parity changes during an optical transition, (ii) the Bloch states are the same for ground and optically excited states, (iii) the $1s$ and np envelopes have opposite parities, and (iv) the nuclear part of the wave function does not participate in optical transitions, then the symmetry of the nuclear part of all the excited states reachable by an optical transition from any state in the ground-state manifold must be unique. In other words, from any of the states whose energy is given by Eq. (7), the accessible states are *either* those given in Eqs. (8) and (10) *or* those states given by Eq. (9), but *not both*.

An analysis of the experimental data^{1,2} shows that, at sufficiently low temperatures, the infrared lines for both the $p_{\frac{3}{2}}$ and for the $p_{\frac{1}{2}}$ series exhibit two peaks or replicas

(equal patterns of peaks) separated by a fixed frequency: $\Delta=38.8\text{ cm}^{-1}$ for (H,Be), and $\Delta=16.2\text{ cm}^{-1}$ for (D,Be). The relative intensity of the lines is temperature independent. These facts indicate that that separation is caused by the structure of the excited states, and not by the properties of the ground-state manifold. Therefore the following points apply.

(i) Since two lines rather than one are observed, if the model with its parity-conservation rule applies then the final states must correspond to the symmetries $(N; \Gamma_1^+)$ and $(N; \Gamma_3^+)$, and not to the symmetry $(N; \Gamma_5^-)$.

(ii) Equations (8a) and (10a) above then uniquely determine the value of $|t|$, which corresponds to 6.5 cm^{-1} for (H,Be), and 2.7 cm^{-1} for (D,Be).

(iii) Equations (8)–(10) clearly show that the two observed lines are thus the *first* and *third* nuclear rotational levels of the complex; the second rotational level is not accessible because of the quasi-parity selection rule.

(iv) The energy separation between first and second levels, given again by Eqs. (8) and (9), are now only $\frac{2}{3}$ of the optically observed splittings, i.e., 25.9 cm^{-1} for (H,Be), and 10.8 cm^{-1} for (D,Be). These values compare well,¹³ within the experimental resolution, with the observed values for the free ions^{2,7} of 21.1 cm^{-1} for (H,Be), and 11.6 cm^{-1} for (D,Be). The model thus solves the inconsistency mentioned in the Introduction.

Transitions within the ground-state manifold are seen in the far-infrared measurements of Ref. 1. For the particular case of (D,Be) the spectra clearly show three peaks (at 5.9, 9.75, and 12.9 cm^{-1}). There are two other small features between these peaks. The tetrahedral model predicted five energy levels in the ground-state manifold, and thus four possible peaks, i.e., transitions from the ground state to all the other states in the manifold; the interpretation located the unseen fourth peak at about 16 cm^{-1} . The present octahedral model also predicts four transitions, even though the number of levels in the manifold has increased from five to eight. Since all the levels have a well-defined parity and optical transitions have a parity selection rule, the possible transitions from the ground state, whatever its symmetry and parity, are only to any of the four states of opposite parity.

A fit of the energy eigenvalues of Eq. (7) to the data yields the following two possible sets of parameters for (D,Be): set 1,

$$t = 2.7\text{ cm}^{-1}, \quad V_0 = -6.3\text{ cm}^{-1}, \quad V_1 = 0.85\text{ cm}^{-1};$$

set 2,

$$t = 2.7\text{ cm}^{-1}, \quad V_0 = 5.9\text{ cm}^{-1}, \quad V_1 = 0.95\text{ cm}^{-1}.$$

Both sets agree with the experimental observations well. In both cases the ground state has Γ_8^- symmetry, which is compatible with the observed splittings of the level under uniaxial stress.² As in the tetrahedral case, a fourth (unidentified) transition is obtained. It occurs at different energies for the two sets: 8.3 cm^{-1} for set 1; 8.7 cm^{-1} for set 2. Regardless of the small difference between the two sets of parameters (0.4 cm^{-1}), the “unidentified” peak falls, for the octahedral model, between the first two “strong” peaks of the spectrum, whereas in the tetrahedral model, as mentioned above, its

frequency is higher than the three observed “strong” peaks.

The infrared experiments also include measurements at higher temperatures,^{1,2} both for the $p_{\frac{1}{2}}$ and the $p_{\frac{3}{2}}$ series. The lower excited states in the ground-state manifold are thermally populated and infrared absorption from these states is observed. As in the case of the ground state, two lines or replicas are observed from the first excited state; one of them is very weak. Only one is seen corresponding to the second excited state.

The tetrahedral model, with the parameters needed to fit the data of Refs. 1 and 2, predicts two lines of comparable magnitude for the ground state, two lines—one strong and one weak—from the first excited state, and a single line from the second excited state, in excellent agreement with experiment. The octahedral model described here gives a ground state of total symmetry Γ_8^- [nuclear symmetry of even (+) parity], a first excited state of symmetry Γ_8^+ , and a second excited state of symmetry Γ_6^+ for set 1 or symmetry Γ_7^+ for set 2. First and second excited states have therefore odd (–) nuclear symmetry parity. Since the Franck-Condon approximation yields conservation of nuclear parity, the octahedral model, as shown in Eqs. (8)–(10), predicts a single absorption line from both thermally populated first and second excited states. If that is the correct interpretation, the weak line observed for the first excited state is misassigned and either belongs to a different series or is spurious.

Since the symmetry of the ground state is of Γ_8 character in both models, they give equally acceptable interpretations for the splitting of optical lines observed under uniaxial stress.

In conclusion, we note the following points.

(1) The model presented here consists of six equivalent positions of the tunneling hydrogen, distributed in an octahedral arrangement (as opposed to four positions in a tetrahedral arrangement). To a very good approximation the Hamiltonian describing such a center has an extra inversion symmetry in the center of mass of the tunneling system, and the wave functions—nuclear, electronic, and total—can thus be classified as even (+) or odd (–).

(2) Although the additional number of sites provide more possible states, the extra symmetry restricts, through parity selection rules, the number of possible optical transitions.

(3) Experimental data for both the far (intra-ground-state $1s$ -envelope manifold) and mid ($1s \rightarrow np$ transitions) infrared can be explained with similar accuracy by either model.

(4) Both models predict an unobserved extra far-infrared line but, whereas the tetrahedral model has it at 16 cm^{-1} , i.e., higher than the three observed lines at 5.9, 9.75, and 12.9 cm^{-1} , the octahedral model predicts it at approximately 8.5 cm^{-1} , between the first and second lines. If observed, this line can serve to distinguish between the models.

(5) The tetrahedral model seems to yield a somewhat better description of the thermally excited absorption from excited states, but the difference resides in the assignment of extremely weak extra lines which may be of

different origin.

(6) The octahedral model, on the other hand, resolves the discrepancy in the frequencies of the nuclear tunneling of the (H,Be) and (D,Be) acceptor complexes in silicon and the rotational frequencies of the corresponding free molecules. The paradox is resolved because the octahedral model contains an unobservable intermediate level, of the opposite parity, between the observed optical frequencies. This parity behavior is similar to that of the free molecule, and produces similar selection rules.

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¹⁰In Ref. 8 Denteneer, Van de Walle, and Pantelides calculate the equilibrium positions of the hydrogen in the various locations allowing, in each case, a complete relaxation of the surrounding atoms. The tunneling paths, however, are calculated assuming no intermediate relaxation of the lattice between

the equivalent initial and final states. Although the BM points, when relaxed, are only 0.1 eV above the *C* minima, in the absence of relaxation their energy is much too high to participate in the tunneling process, which may proceed instead through the antibonding directions.

¹¹The octahedral model developed here requires only eight quantum nuclear states with matrix elements compatible with octahedral symmetry and permitting “tunneling” among them; the specific mechanisms of tunneling as well as the presence or absence of relaxation of the various atoms and configurations are essentially irrelevant for the analysis carried out here.

¹²It should be noted that the excited states of the *np* manifold actually do split into states of symmetries Γ_8 , Γ_8 , Γ_6 , and Γ_7 for $p_{\frac{3}{2}}$, and Γ_6 and Γ_8 for $p_{\frac{1}{2}}$; this splitting is observed experimentally but is irrelevant for the present discussion.

¹³The obtained value for the $(N; \Gamma_1^+)$ to $(N; \Gamma_5^-)$ level separation for H, 25.9 cm^{-1} , is still *larger* than the molecular rotation splitting of 21.1 cm^{-1} . The difference is nonetheless small, the lines are fairly broad, and inclusion of second-neighbor tunneling should alter slightly the ratio of 2:1 between the Γ_1^+ to Γ_5^- and Γ_5^- to Γ_3^+ energy separations.